

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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 (72) Inventor JOSEPH LEE RUSSELL



(54) PROCESS FOR THE ACYLOXYLATION OF OLEFINS

(71) We, HALCON INTERNATIONAL INC. of 2 Park Avenue, New York, New York 16, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a continuous vapor phase catalytic process for the acyloxylation of olefins (*i.e.*, the addition of an R-CO-O- radical to an olefin, where R is a hydrocarbon radical) whereby unsaturated esters of carboxylic acids are produced, the unsaturation being that of the olefin starting material. In a preferred embodiment, this invention relates to the acetoxylation of olefins and, in an especially preferred embodiment, this invention relates to the production of vinyl acetate from ethylene and acetic acid.

The process of this invention permits obtaining higher yields of acyloxylation of olefins (*i.e.*, unsaturated esters of carboxylic acids) than heretofore deemed practicable in commercial operation of such processes. This is accomplished by conduct of the acyloxylation reaction in at least two stages. The first stage is operated to obtain maximum reaction selectivity while, in subsequent stages, olefin conversion is maximized.

In recent years olefinic esters of carboxylic acids, such as, for example, vinyl acetate, allyl acetate, and the like, have become increasingly important articles of commerce. Such materials are monomers for the production of commercially important resins, *e.g.*, in the case of vinyl acetate, such resins as polyvinyl acetate, polyvinyl alcohol and polyvinyl acetals. Traditionally, such olefinic esters have been

made by the catalytic vapor phase reaction of acetylenic derivatives with an organic acid, which has been disadvantageous because requiring use of relatively expensive acetylenic compounds as reactants. Accordingly, evermore attention is being directed to alternative processes employing olefin acyloxylation techniques.

According to British Patent No. 796,613, olefinic esters (such as vinyl acetate) are formed by passing a gaseous reaction mixture comprising a carboxylic acid, an olefin and molecular oxygen through a reactor containing a noble metal catalyst. Such a process, however, has the drawback of being only a partial conversion one, and olefin yields per pass are low. To overcome this disadvantage in commercial operation, it is accordingly necessary that unreacted olefin and carboxylic acid be recycled. Prior art efforts to minimize the size and cost of recycle facilities (by maximizing conversion) have proved self-defeating since efficiency of the prior art processes has decreased as conversion was increased. Recycle too causes disadvantages since a portion of the materials which otherwise would be recycled must be purged in an amount corresponding in volume to the volume of the new components to be added to the reaction system as fresh feed less that withdrawn as product. The amount of olefin and carboxylic acid lost in such a purge seriously lowers the efficiency of the process. In contrast, this invention provides a process having significantly enhanced yields over those obtained in prior art process.

This invention relates to the acyloxylation of olefins to produce unsaturated esters of carboxylic acids. The process of this invention is continuous, is conducted in the vapor phase and comprises contacting a gaseous mixture containing molecular oxygen, olefin to be acyloxylation and

- carboxylic acid with a first body of catalyst at a temperature in the range of from 50 to 350°C at a space velocity of from 20 to 5000 hr.⁻¹ to give a conversion of olefin in the range of from 4 to 20%;
- 5 removing acyloxylated olefin from the resulting mixture;
- 10 purging a portion of the remaining mixture;
- 10 recycling the portion of the mixture remaining after purging for further contact with said first catalyst;
- 15 contacting the purged gaseous mixture with a second body of catalyst, said contacting being carried out at a temperature in the range of from 50 to 350°C at a space velocity from 20 to 5000 hours⁻¹; and
- 20 recovering additional acyloxylated olefin, both said first and second bodies of catalyst comprising a Group VIII metal having an atomic number of at least 44.
- From about 30 to about 80% of the olefin in the purge gas may be converted.
- 25 The balance of the effluent from the second contact step, after the effluent has been treated for the recovery of additional acyloxylated olefin, may be recycled to the second contact step, with a portion of the recycled material, equal in volume to
- 30 the volume of material purge from the first contacting step less the volume withdrawn as product, being purged.
- The aforementioned conditions are such
- 35 that the first catalyst contact step is operated under conditions such as to give high selectivity to formation of the acyloxylated olefin. The second catalyst contact step is operated such as to give high conversion.
- 40 The process of this invention also encompasses a system employing three or even more catalyst contact steps, the first being substantially as described above, the second being operated in such a manner
- 45 as to obtain moderate conversion at moderate selectivities with the third and any subsequent catalyst contact steps being operated so as to obtain high conversions.
- 50 All catalyst contact steps employ a solid catalyst comprising a noble metal. These metals can be used as such or they can be used in supported form employing such inert support materials as titania, silica
- 55 and alumina.

DEFINITIONS

- As hereinabove and as hereinafter used in this specification and as used in the appended claims, the following terms have the following meanings unless otherwise indicated;

The term "selectivity" designates the ratio, expressed on a molar basis, of

$$\frac{\text{acyloxylated olefin formed}}{\text{mole of olefin reacting}}$$

65

By "high" selectivity is meant a selectivity, as defined hereinabove, which is above about 0.75 or, expressed as a percentage, above about 75%. By "moderate" selectivity is meant one which is above about 65%.

The term "conversion" designates the ratio, expressed on a molar basis, of

75

$$\frac{\text{moles of olefin feed which react}}{\text{moles of olefin fed}}$$

The term "conversion per pass" refers to the conversion, as hereinabove defined, on a once-through basis, i.e., not taking recycles into account. By "high" conversion is meant a conversion which is above about 0.30 or, expressed as a percentage, above about 30%. By "moderate" conversion is meant one which is above 15% but below about 30%. By "low" conversion is meant one which is below about 15%.

The term "yield" designates the ratio, expressed on a molar basis, of

90

$$\frac{\text{moles of acyloxylated olefin formed}}{\text{moles of olefin feed}}$$

95

It is to be noted that the above definitions of "selectivity", "conversion" and "yield" are based upon olefin. It would be equally possible to define these in terms of carboxylic acid fed and reacting; however, under the conditions employed in the process of this invention, selectivities of formation of acyloxylated olefin based on carboxylic acid reactant are too high to make definitions based on acid meaningful. Conversions of acid, of course, vary in direct relation to olefin conversion.

100

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As used herein, the term "space velocity" is defined as the quotient obtained by dividing the volume of total feed (fresh plus recycle) to a reactor per hour by the volume of catalyst contained within the reactor. Since reactor feeds in the process of this invention are gaseous, feed volumes are calculated at standard conditions (0°C and 760 mm Hg. absolute).

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The term "acyloxylation" as herein used refers to a reaction resulting in the

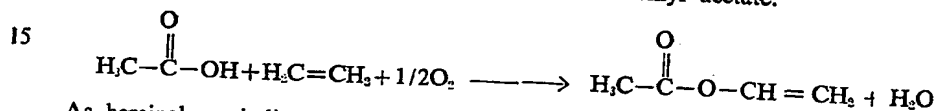
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addition of the organic radical R-C-O-, where R is a hydrocarbon radical, to an organic material by replacement of a hydrogen atom of the organic material. In this invention, the organic material is an

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olefin and the $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-$ radical is added thereto in such manner as not to destroy the double bond of the olefin feed material. This reaction can perhaps best

be understood by consideration of the following chemical equation which employs for purposes of illustration but not as limitative of this invention, the reaction between acetic acid, ethylene and oxygen to form vinyl acetate.



As hereinabove indicated the process of this invention involves an acyloxylation reaction employing three raw materials, viz., an olefin, a carboxylic acid and molecular oxygen. These materials are contacted with a noble/metal catalyst (as hereinafter more fully described) and in part reacted to form acyloxylation products. Since, in this reaction, conversions per pass above about 20% cannot be obtained without uneconomically low selectivities, in continuous operation it is necessary to recover and recycle unreacted olefin and carboxylic acid to improve process economics. But as pointed out above, this necessitates purging a portion of the recovered, unreacted feed materials, after recovery and withdrawal of acyloxylation olefin product, to provide for fresh make-up feed stocks.

It is the essence of this invention that the purge material be subjected to a secondary contacting step with a second body of noble metal catalyst. Provision of such a secondary contacting step (sometimes referred to herein as a "purge reaction system") allows operation of the first contacting step (sometimes herein referred to as a "main reaction system") in such manner as to maximize selectivity therein which, in turn, necessitates lower conversions per pass than would otherwise be the case. In combination with this step, the purge gases are subjected to a secondary acyloxylation reaction under conditions maximizing overall conversion.

Control of conversion, and hence of selectivity, is obtained by appropriate adjustment of reaction conditions in both the main reaction and purge reaction systems. The reaction conditions in each stage which are independently controllable are temperature and pressure, reactor feed composition and catalyst space velocity (which is equivalent to residence time). Suitable reaction conditions for obtaining maximum selectivity in the main reaction system include a temperature within the range of from 50 to 350°C., desirably within the range of from 50 to 250°C. and preferably within the range of from 100 to 200°C. Suitable pressures are between 1 and 200 atmospheres and preferably within the

range of from 1 to 50 atmospheres.

Suitable total feed composition (fresh feed plus recycle) for the main reaction system include feeds having an olefin concentration between 5 and 85% by volume, a carboxylic acid content between 5 and 65% by volume, and an oxygen content consistent with safe operation of the particular system at the temperature and pressure employed, i.e., oxygen contents should be maintained below the lower explosive limit.

Space velocities of between 20 and 5000 hours⁻¹ at the aforesaid temperatures and pressures in ethylene acyloxylation will result in conversions per pass of from 4 to 20% corresponding to selectivities of from 75 to 90%. It will be noted that these conversions per pass are quite low but that the selectivity obtained is high.

As hereinabove indicated, a portion of the reaction effluent containing unreacted olefin and carboxylic acid is purged from the main reaction system recycle stream and is treated in the purge reaction system under conditions adapted to give high conversions albeit with low selectivity. Suitable purge reaction system conditions include a temperature within the range of from 50 to 350°C., desirably within the range of from 50 to 250°C., and preferably within the range of from 100 to 200°C. Suitable pressures are from 1 to 200 atmospheres and preferably between 1 and 50 atmospheres. Suitable total feed compositions (fresh feed plus recycle) for the purge reaction system include feeds having olefin concentration between 5 and 85% by volume, a carboxylic acid content between 5 and 65% by volume, and an oxygen content consistent with safe operation of the particular system at the pressure and temperature employed. When the olefin is relatively volatile, e.g., ethylene or propylene, and where no subsequent contacting stages are used, the olefin content of the reactor feed is preferably maintained at a sufficiently low level that it is not important to process economics to recover olefin from the plant purge. Space velocities between 20 and 5000 hours⁻¹ at the aforesaid temperatures and pressures will result in conversions per pass of from 30 to 80%.

The process of this invention, as hereinabove described, is applicable to the acyloxylation of a variety of olefin feed materials. Suitable olefins are those having from 2-18 carbon atoms such as, for example, ethylene, propylene, butene-1, butene-2, isobutylene, the n-amylenes, the isoamylenes and hexenes, methylpentenes, dodecenes and octadecenes. Olefins having aliphatic, aromatic and alicyclic substituents are also suitable such as, for example, styrene and 3-cyclohexylpropylene. The preferred olefins are ethylene and propylene.

Similarly, the process of this invention employs a variety of carboxylic acids as feed materials for the acyloxylation reaction. Suitable carboxylic acids are those having from 1-18 carbon atoms per molecule although those having 10 or less carbon atoms per molecule are preferred since these are more readily volatilized. Aliphatic, alicyclic and aromatic carboxylic acids are all suitable raw materials for the practice of this invention. Thus, suitable acids include formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, capric acid, myristic acid and benzoic acid. Acetic and propionic acids are preferred.

It should be recognized that mixtures of olefins or mixtures of carboxylic acids or both can be employed. However, in such cases mixtures of acyloxyated olefin products rather than single compound products will be obtained.

As hereinabove indicated, the acyloxylation is a heterogeneous catalytic reaction involving the use of a solid catalyst. Suitable solid catalysts are the metals of Group VIII of the periodic table which have atomic numbers of 44 or more, viz., ruthenium, rhodium, palladium, osmium, iridium and platinum. These metals can be used as such or they can be deposited on a support in the form of their compounds, most suitably the form of their acetates, propionates or other lower aliphatic carboxylic acid salts (having from 1-6 carbon atoms) or as the oxides or halides and then reduced, *in situ*, at least in part, to the metallic state. The metals (or reduced metal compounds) can be supported or unsupported. Suitable supports include titania, silica, alumina, carbon, magnesia, zirconia and magnesia-zirconia spinels. Advantageously, a small amount, up to 5% by weight of the Group VIII metal, of a promoter can be added to the catalyst. Suitable promoters are salts of the alkali metals such as the acetates and propionates. Sodium, lithium and potassium salts are preferred. A particularly satisfactory catalyst contains 2 wt % palladium and 2 wt % sodium acetate

deposited upon a spinel support, palladium being deposited on the support as palladium chloride which is then reduced, at least in part, to the finely divided metallic state by alkali plus hydrazine, alkaline formaldehyde or hydrogen.

Any source of molecular oxygen can be used as a raw material for the process of this invention. Air is normally preferred as it is least expensive although the use of air necessitates a higher purge rate to prevent the build-up of nitrogen in the main reactor recycle system to too high a concentration. However, the process of this invention also encompasses the use of high purity oxygen streams as well, up to, say, 80% oxygen or even more.

Acyloxyated olefin product is readily recovered from the reactor effluent in known manner as by, for example, scrubbing of the reactor effluent with a solvent for the acyloxyated olefin, e.g., acetic acid, and then recovering the olefin ester by distillation of the solvent-ester solution or by condensation or decantation followed by distillation or by combinations of these methods or otherwise.

DRAWING

The process of this invention will be more fully explained in conjunction with the attached drawing which is a schematic representation of one embodiment of this invention employing a main reaction system and a purge reaction system.

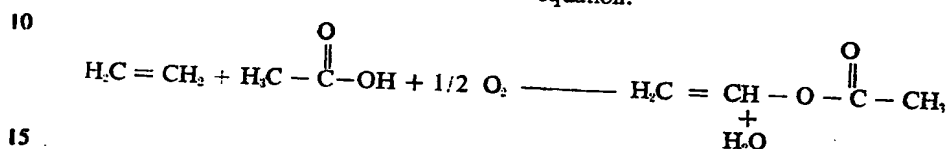
For ease of discussion of the embodiment illustrated by the accompanying drawing, but without intending to limit the scope of the invention thereby, the feed to the process illustrated in the drawing is assumed to be ethylene and acetic acid plus, of course, oxygen and the product obtained is therefore vinyl acetate.

Fresh ethylene feed is introduced to reactor 10 via conduit 11. Fresh, vaporized acetic feed and molecular oxygen, preferably in the form of air, are introduced to reactor 10 via conduits 12 and 13 respectively. A recycle stream containing ethylene, acetic acid and possibly also containing some molecular oxygen together with other materials, such as by-product carbon dioxide formed in the reaction, is introduced to reactor 10 via conduit 14. The manner in which this recycle stream is obtained will be hereinafter described.

Disposed within reactor 10 is a solid, noble metal catalyst which advantageously can comprise palladium deposited on a support, e.g., a magnesia-zirconia spinel. Reactor 10 is preferably of the fixed bed type and the catalyst can be disposed in a single bed or in a plurality of beds contained therewith. Reactor 10 can also be of the tubular type, i.e., one which has a

plurality of catalyst-containing tubes surrounded by a fluid heat transfer medium. All such reactors are of types known to those skilled in the art.

Within reactor 10 the reactants combine to form vinyl acetate and water in accordance with the following chemical equation:



- Since the above reaction is exothermic, it is desirable though not essential that provision be made for removing the heat of reaction. This can readily be accomplished by means known to those skilled in the art, such as, for example, by the provision of cooling coils 15 disposed within reactor 10.
- The reaction products, by-products and unreacted feed materials are withdrawn from reactor 10 via conduit 16. This reactor effluent is cooled in heat exchange unit 17 and introduced to separation unit 20. Separation unit 20 desirably is an absorption column of the tray type or of the packed column type (e.g., containing Raschig rings). Within separation unit 20, readily condensable materials such as the vinyl acetate product, unreacted acetic acid and the like are separated from relatively non-condensable materials, such as unreacted ethylene and nitrogen associated with the air used as the source of molecular oxygen, by scrubbing the reactor effluent with an absorbant for vinyl acetate, suitably acetic acid. The absorbent is introduced to the upper portion of separation unit 20 via conduit 21. Vinyl acetate, unreacted acetic acid and acetic acid absorption agent are withdrawn from the lower portion of separation unit 20 via conduit 22 and are sent to fractionation unit 30.
- Non-condensable materials such as unreacted ethylene, carbon dioxide by-product, nitrogen introduced to reactor 10 in the form of air and the like are withdrawn from the top of separation unit 20 via conduit 23. A portion of this non-condensable material is recycled to reactor 10 via conduits 24 and 14 after compression in vapor compression unit 25. Reactor 10, separation unit 20 and vapor compression unit 25 are sometimes hereinafter referred to as the "main reactor system."
- The balance of the vapor material withdrawn from separation unit 20 via conduit 23 is purged from the main reactor system via conduit 26 and is processed in a manner to be subsequently described.
- The condensed materials withdrawn from separation unit 20 via conduit 22 are treated in fractionation unit 30 to separate and recover vinyl acetate and acetic acid. Fractionation unit 30 is a distillation type known to those skilled in the art and is equipped with a plurality of vapor-liquid contacting devices and suitable reflux and re-boiling systems (not shown). Vinyl acetate product is withdrawn from the overhead of fractionation unit 30 via conduit 31 and can be further purified, if desired, in known manner. Acetic acid together with by-products is withdrawn from a lower portion of fractionation unit 30 via conduit 32 and is divided into two streams. One portion of the recovered acetic acid is cooled in heat exchanger 38 and returned to separation unit 20 via conduit 21 where it is employed as the absorption agent. The balance is vaporized in vaporizer 34 and, after vaporization, is also divided into two streams. A portion is recycled to reactor 10 via conduits 35 and 14. The balance is purged from the system via conduit 37.
- Purged ethylene from conduit 26 and purged acetic acid from conduit 37 are admixed and introduced to purge reactor 40 via conduit 39. Additional molecular oxygen, preferably in the form of air, also is introduced to purge reactor 40 via 42. Additional acetic acid and/or ethylene can also be introduced if desired via suitable conduits (not shown). Purge reactor 40 can be of the same type as purge reactor 10 and advantageously is also equipped with cooling coils 43. A recycle stream obtained in a manner hereinafter described is introduced to purge reactor 40 via conduit 44. In purge reactor 40 additional vinyl acetate is formed according to the chemical reaction hereinabove presented.
- The reaction products together with unreacted materials are withdrawn from purge reactor 40 via conduit 45, cooled in heat exchanger 46 and introduced to a lower portion of separation unit 50 which is of the same type as separation unit 20. Absorbant, suitably acetic acid, is introduced to an upper portion of separation unit 50 via conduit 51. Vinyl acetate and acetic acid withdrawn from purge reactor 40 are absorbed and removed from the

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bottom of separation unit 50 via conduit 52 and are sent to fractionation unit 60. Non-condensed material, including unreacted ethylene, are withdrawn from separation unit 50 via conduit 53 and are divided into two streams. A portion is recycled to purge reactor 40 via compressor 54, the discharge of which communicates with conduit 44. The balance is purged from the system via conduit 55 and discarded.

The liquid stream withdrawn from separation unit 50 via conduit 52 is processed in fractionation unit 60, which is of the same type as fractionation unit 30, to separate vinyl acetate product from acetic acid. Vinyl acetate product is withdrawn from the overhead of fractionation unit 60 via conduit 61 and, if desired, can be subjected to known purification techniques. Acetic acid, substantially free of vinyl acetate, is withdrawn from the bottom of fractionation unit 60 via conduit 62 and divided into two streams. A portion is cooled in heat exchanger 59 and returned to separation unit 50 via conduit 51 to serve as the absorption agent. A portion of the remainder is purged via conduit 63 and discarded. The balance is vaporized in heat exchanger 64 and recycled to purge reactor 40 via conduit 65.

EXAMPLE

The following example is presented to illustrate this invention but is not intended as limiting the scope thereof. For this purpose, the reaction of ethylene, oxygen, and acetic acid to form vinyl acetate is again employed. Air is used as the source of molecular oxygen. Unless otherwise indicated, all parts and percentages in the following example are on a molar basis.

A reaction system similar to that schematically depicted in the annexed drawing is set up for the purpose of continually acetoxyating ethylene therewithin. The following discussion relates to the operations of this system after steady state conditions are attained.

A gaseous reaction mixture of air, ethylene, acetic acid and recycle gas, which reaction mixture has the following composition, is fed to the main reactor at a rate of 100 parts per hour:

	Ethylene	10.8%
	Acetic Acid	4.2%
55	Carbon dioxide	3.0%
	Nitrogen	75.0%
	Oxygen	7.0%
	Vinyl acetate	—
60	Water	—
		100.0%

Within the main reactor are disposed 1300 parts (by weight) of a catalyst containing 2 wt.% palladium and 2 wt.%

sodium acetate deposited on a magnesia-zirconia spinel support, the palladium being deposited upon the support in the form of palladium chloride which is then reduced, at least in part, to the metallic state by treatment with a mixture of sodium hydroxide plus hydrazine. This quantity of catalyst in conjunction with the above feed rate corresponds to a space velocity of 2200 volumes of feed per hour per volume of catalyst. Main reactor temperature is maintained at 120°C. and pressure is maintained at 75 psig.

After each reaction the material leaving the main reactor contains:

	9.720 parts/hr	80
Ethylene	3.304 "	
Acetic Acid	3.368 "	
Carbon dioxide	75.000 "	
Nitrogen	6.000 "	85
Oxygen	0.896 "	
Vinyl acetate	0.368 "	
Water		

From the above, it can be seen that conversion per pass of ethylene is 10% and selectivity to vinyl acetate is 83%. Vinyl acetate is recovered and 6.983 parts per hour of a purge of the following composition (dry basis) is taken:

Ethylene	9.98%	95
Acetic Acid	3.39%	
Carbon dioxide	3.45%	
Nitrogen	77.02%	
Oxygen	6.16%	
Vinyl acetate	—	100
		100.00%

The balance of the reactor effluent (90.40 parts/hr.) excluding recovered vinyl acetate, is recycled to the main reactor.

Inspection of the hereinabove presented data will indicate that the overall conversion of ethylene to vinyl acetate monomer in the main reactor system is 60.8% and that the overall main reactor yield is 50.46%.

To the main reactor purge (6.983 parts/hr.) is added 4.782 parts/hr. of air and 0.219 parts/hr. of acetic acid together with the purge recycle gas and introduced to the purge reactor. The overall feed to the purge reactor has the following composition:

	1.29 parts/hr.	
Ethylene	0.52 "	120
Acetic Acid	6.45 "	
Carbon dioxide	112.17 "	
Nitrogen	8.51 "	
Oxygen	—	125
Vinyl acetate	—	
Water		

Disposed within the purge reactor are 2500 parts (by weight) of a catalyst identical with that used in the main reactor.

This amount of catalyst provides a space velocity of 1450 volumes of feed per hour per volume of catalyst. Purge reactor conditions are maintained at 130°C. and 75 psig. The effluent from the purge reactor has the following composition:

	Ethylene	0.64 parts/hr
	Acetic Acid	0.06 "
	Carbon Dioxide	6.83 "
10	Nitrogen	112.17 "
	Oxygen	7.71 "
	Vinyl acetate	0.45 "
	Water	0.39 "

128.25 parts/hr.

After recovery of additional vinyl acetate from the purge reactor effluent, 10.43 parts/hr. of the remaining material is purged from the system and discarded. The balance is recycled to the purge reactor.

Inspection of the above data indicates that purge reactor conversion is 50% while selectivity is only 70%. However, the overall conversion in main plus purge reactor is 97% and the overall yield is approximately 75.7%. Hence it will be seen that the overall yield of the process of this invention is increased by over 25 percentage points in comparison with the case where no purge reactor is used. It is therefore clearly evident that the method of this invention provides major economic advantages over conventional processes employing but one reactor.

The foregoing description illustrates the methods of this invention whereby the advantages thereof are obtained. It will be understood that modifications and variations thereof may be effected by those skilled in the art. For example, it is not necessary that but a single purge reactor be used. It is evident that the material discarded from the purge reactor effluent can readily be processed in an additional reactor to further increase overall yield. Accordingly, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

WHAT WE CLAIM IS:—

1. A continuous process for the production of acyloxyated olefins which comprises:

(a) contacting a gaseous reaction mixture containing molecular oxygen, olefin to be acyloxyated and carboxylic acid with a first body of catalyst, said contacting being carried out at a temperature within the range of from 50 to 350°C at a space velocity from 20 to

5000 hours⁻¹ whereby a conversion of olefin within the range of from 4% to 20% is obtained;

(b) removing acyloxyated olefin from the resulting mixture;

(c) purging a portion of the remaining mixture;

(d) recycling the portion of the mixture remaining after purging for further contact with said first catalyst;

(e) contacting the purged gaseous mixture with a second body of catalyst, said contacting being carried out at a temperature in the range of from 50 to 350°C at a space velocity from 20 to 5000 hours⁻¹; and

(f) recovering additional acyloxyated olefin, both said first and second bodies of catalyst comprising a Group VIII metal having an atomic number of 80 at least 44.

2. A process according to claim 1, in which step (a) is carried out at a temperature of from 100 to 200°C.

3. A process according to claim 1 or claim 2, in which step (a) is carried out at a pressure of from 1 to 50 atmospheres.

4. A process according to any preceding claim, in which the gaseous reaction mixture in step (a) comprises from 5 to 85% by volume of olefin and from 5 to 65% by volume of carboxylic acid.

5. A process according to any preceding claim, in which step (e) is carried out at a temperature of from 100 to 200°C.

6. A process according to any preceding claim, in which step (e) is carried out at a pressure of from 1 to 50 atmospheres.

7. A process according to any preceding claim, in which the carboxylic acid has from 1 to 10 carbon atoms.

8. A process according to any preceding claim, in which the Group VIII metal is palladium.

9. A process according to any preceding claim, in which the olefin is ethylene, the carboxylic acid is acetic acid and the acyloxyated olefin is vinyl acetate.

10. A process for producing an acyloxyated olefin substantially as hereinbefore described and exemplified.

11. An acyloxyated olefin when produced by the process of any preceding claim.

MATHYS & SQUIRE,
Chartered Patent Agents,
10 Fleet Street,
LONDON, E.C.4.
Agents for the Applicants.

1,264,377 COMPLETE SPECIFICATION

1 SHEET

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